

# PATENT SPECIFICATION

(11) 1 581 379

1 581 379

- (21) Application No. 52749/77 (22) Filed 19 Dec. 1977  
 (31) Convention Application No. 755122  
 (32) Filed 28 Dec. 1976 in  
 (33) United States of America (US)  
 (44) Complete Specification published 10 Dec. 1980  
 (51) INT Cl<sup>3</sup> C07C 31/20  
 (52) Index at acceptance  
 C2C 20Y 21X 30Y 360 361 362 36Y 50Y 569 607 633 65Y FF YN  
 (72) Inventor RICHARD E. ERNST



## (54) PREPARATION OF DIOLS BY HYDROGENATION AND HYDROLYSIS OF CYCLIC ACETALS

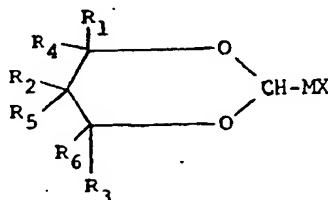
(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the simultaneous catalytic hydrolysis and hydrogenation of cyclic acetals. More specifically, this invention relates to a process for the simultaneous catalytic hydrolysis and hydrogenation of cyclic acetals carried out at a pH of at least 4.0.

The preparation of diols from cyclic acetals is known. However, the methods used have experienced unsatisfactory catalyst life, especially where the hydrogenation catalyst is not a noble metal and where the hydrolysis and hydrogenation are conducted simultaneously. U.S. Patent 2,888,492 discloses the simultaneous hydrolysis and hydrogenation of certain hydroxy aldehydes in the presence of an aqueous acidic medium and a hydrogenation catalyst. However, in such cases when a base metal hydrogenation catalyst is used the catalyst life is unsatisfactorily low. U.S. Patent 2,618,663 discloses the simultaneous hydrolysis and reduction of polyether alkanol acetals to the corresponding polyether alcohols by carrying out said simultaneous hydrolysis and reduction in an aqueous solution containing catalytic quantities of hydrolyzable metal salts of mineral and organic acids with Raney nickel catalyst and hydrogen at a pH of 4.5 to 5.5 to minimize corrosion of the equipment. U.S. Patent 3,886,219 discloses a process for the preparation of saturated aliphatic alcohols by the hydrogenation of saturated or unsaturated aldehydes and/or ketones in the presence of catalysts supported on silica gel having a surface pH of 6 to 10. U.S. Patent 3,492,314 discloses the hydrogenation of succinic anhydride in the presence of a reduced nickel-rhenium catalyst to improve the catalyst life. However, there is still a need to further improve the performance of catalysts in hydrogenation/hydrolysis reactions.

Now it has been found that the catalyst life in hydrolysis and hydrogenation reactions of cyclic acetals to 1,4-butanediol is extended by conducting said reactions at a pH of at least 4.0.

In accordance with the invention, a process has been found for the simultaneous catalytic hydrolysis and hydrogenation of a cyclic acetal of the general formula

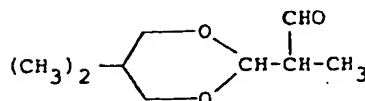
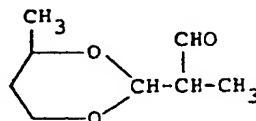
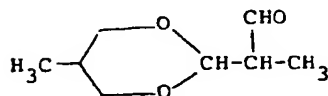
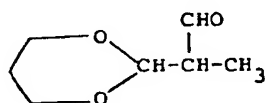
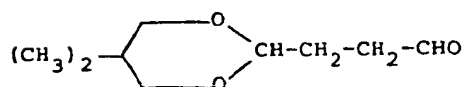
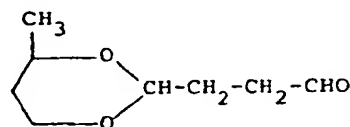
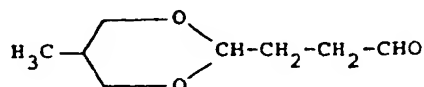
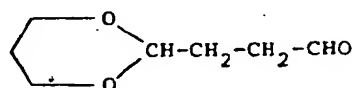
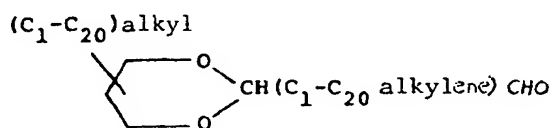


and mixtures thereof

wherein M is an alkylene group of 1 to 20 carbon atoms, X is —CHO or —CH<sub>2</sub>OH and R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub> may be the same or different hydrogen or alkyl

groups of 1 to 20 carbon atoms which comprises hydrolyzing and hydrogenating said cyclic acetal at an elevated temperature under superatmospheric hydrogen pressure in the presence of both an aqueous acid solution and a base metal hydrogenation catalyst at a pH of 4.0 or more until a product comprising a diol or mixture of diols is produced.

Some specific examples of cyclic acetals which may be hydrolyzed and hydrogenated in accordance with this invention include



and the corresponding alcohols (where —CHO is replaced with CH<sub>2</sub>OH).

In the process of this invention, any catalytic amount of any of the metal or metal compound catalysts of the type well known and customarily referred to in the art as base metal hydrogenation catalysts can be used. The base metal hydrogenation catalyst may be a metal, a mixture of metals or a compound of a metal wherein the metal(s) oxidizes rapidly and the hydroxide of the metal(s) is soluble in water. Representative examples of such base metal hydrogenation

catalysts include nickel, conventional Raney nickel, conventional Raney nickel promoted with molybdenum, conventional Raney nickel promoted with chromium, granular foraminous nickel, granular foraminous nickel activated with molybdenum, chromium, cobalt or chromium and molybdenum.

What is meant by conventional Raney nickel is an alloy of nickel and aluminum wherein the aluminum is 50 to 70% by weight and wherein essentially all of the aluminum that can be removed by normal means is removed.

What is meant by granular foraminous nickel is a free-standing granular alloy of the Raney nickel type with 50 to 70% by weight aluminum which has from 10 to 50% of the aluminum removed from the alloy.

What is meant by conventional Raney nickel activated with either molybdenum or chromium is an alloy of nickel, aluminum and chromium or molybdenum wherein 1 to 10% by weight is chromium or molybdenum, 50 to 70% by weight is aluminum and 49 to 20% by weight is nickel and wherein essentially all of the aluminum that can be removed by normal means is removed.

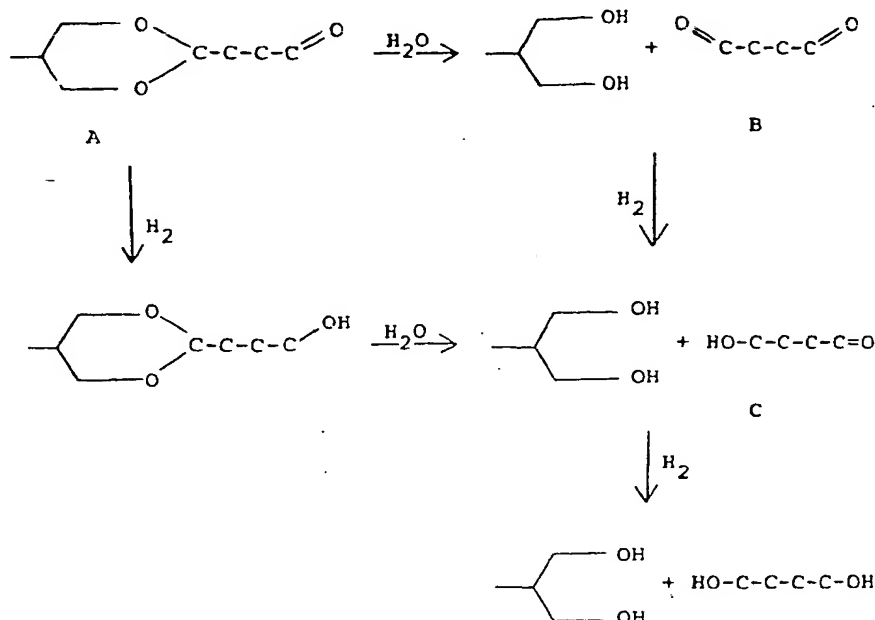
What is meant by granular foraminous nickel activated with either molybdenum or chromium is a free-standing alloy of the Raney nickel type with 50 to 70% by weight aluminum, 49 to 20% by weight nickel and 1 to 10% chromium or molybdenum which has from 10 to 50% of the aluminum removed from the alloy.

The aluminum is generally removed from the alloy with an aqueous alkali metal hydroxide solution until the desired amount of aluminum is leached from the alloy. The alkali metal hydroxide solution will generally contain about 0.1 to 5% by weight of alkali metal hydroxide. When more than about 50% of the aluminum is removed, the mechanical strength of the nickel-aluminum catalyst particles is reduced such that they are no longer suitable for use in a fixed bed. Representative examples of metal compounds within the scope of this invention include copper chromite. The preferred base metal hydrogenation catalysts are selected from the group consisting of nickel, granular foraminous nickel, conventional Raney nickel, conventional Raney nickel promoted with either chromium or molybdenum and granular foraminous nickel promoted with either chromium or molybdenum. Most preferred are granular foraminous nickel, conventional Raney nickel, granular foraminous nickel promoted with molybdenum or chromium and conventional Raney nickel promoted with molybdenum or chromium.

The chromium nickel and molybdenum nickel mixtures or alloys are available commercially from Davison Chemical, a division of W. R. Grace and Company. Chromium promoted nickel and molybdenum promoted nickel are the most active of the hydrogenation catalysts mentioned herein.

In the process of the present invention, it was found that in the stream being hydrogenated a more active catalyst will increase the conversion of the cyclic acetal to the diol or diols. It was found that catalysts which are less active do not promote sufficiently high conversion and result in the preparation of more undesirable byproducts. The chromium-promoted nickel and more especially the molybdenum-promoted nickel result in rapid hydrogenation and low undesirable byproducts. In the hydrogenation/hydrolysis reaction of this invention, it is essential in order to attain low undesirable byproducts that the hydrogenation be conducted as fast as possible to avoid competing reactions of the aldehyde formed by hydrolysis. The presence of said aldehydes will promote the formation of undesirable byproducts. For example, molybdenum nickel catalyst in the process of the present invention results in less undesirable byproducts than Raney nickel because of its superior hydrogenation activity.

The following equations describe the formation believed to contribute to undesirable byproducts that are minimized with active hydrogenation catalysts:



The aldehyde groups in A, B and C undergo reactions producing undesirable byproducts unless these aldehyde groups are hydrogenated rapidly to alcohol groups.

Hydrogenation reactions generally do not require any high degree of hydrogenation to prevent undesirable byproduct formation.

The base metal hydrogenation catalyst may be employed in a finely divided form or slurry without a support and dispersed in and throughout the reaction mixture, or it may be employed in a granular form with aluminum as a support or in a more massive state, either in essentially the pure state or supported upon or carried by an inert or catalytically active supporting or carrier material, such as pumice, kieselguhr, diatomaceous earth, clay, alumina, charcoal, carbon, or the like, and the reaction mixture contacted therewith as by flowing the mixture over or through a bed of the catalyst or according to other methods that are known in the art.

In the process of this invention rhenium or a rhenium compound may optionally be used as a component of the base metal hydrogenation catalyst for the purpose of further extending the life of said catalyst. The rhenium modified base hydrogenation catalysts of this invention may be prepared by adding a solution of  $\text{Re}_2\text{O}_7$  in water to, e.g., nickel on alumina. The nickel on alumina absorbs the rhenium and the resulting catalyst is placed in a reactor and treated with  $\text{H}_2$  at a temperature and pressure and for a time that will reduce and insolubilize the  $\text{Re}_2\text{O}_7$ , e.g., at 1 atmosphere and  $180^\circ\text{C}$  for 2 hours.

The hydrogenation and hydrolysis of this invention is carried out at an elevated temperature under superatmospheric hydrogen pressure and in the presence of an aqueous medium as well as in the presence of an acid hydrolysis catalyst and the base metal hydrogenation catalyst. Generally, the amount of water present is that amount that is sufficient for the hydrolysis/hydrogenation step; that is, a molar ratio of water to acetal of 1:1 to 100:1, preferably 1:1 to 10:1. The hydrogen pressure is generally from 500 to 10,000 psig, preferably 1,000 to 5,000 psig. The temperature is generally  $125^\circ$  to  $200^\circ\text{C}$ , preferably  $125^\circ$  to  $175^\circ\text{C}$ .

The hydrolysis portion of the process of the present invention requires an acid catalyst. In view of the requirement that water be present for the hydrolysis, the acid is present as an aqueous acid. The aqueous acid for the hydrolysis reaction may be selected from a wide variety of acid-reacting materials and can be used for imparting the required acidity to said aqueous reaction medium. Acids and acid-reacting salts have both been successfully used. Mineral acids such as sulfuric, phosphoric and the like acids or such acid-acting salts as sodium bisulfate, monosodium orthophosphate, aluminum sulfate and the like may be used in the

process of the present invention. Water-soluble organic carboxylic acids are also acidifying agents for use in the process of this invention. Particularly useful are the lower fatty acids of 1 to 4 carbon atoms, especially acetic, propionic, isobutyric and normal butyric acids but polycarboxylic acids such as succinic, malonic, and adipic acids are suitable. These organic acids are useful in amounts of about 5 to 100% by weight of the water used in the reaction. However, a normality of from about 0.005 to about 1 is preferred. Insoluble acid ion exchange resins may also be used in the process of the present invention.

In the preparation of the cyclic acetals of the aforesaid general formula there is normally sufficient acid present with the cyclic acetal to not require the addition of acid beyond that present thereby. Thus normally in order to maintain the pH within the invention, it is necessary to add caustic. Any caustic solution may be used. However, because of availability and convenience sodium hydroxide and potassium hydroxide are preferred.

The pH of the reaction mixture for the simultaneous hydrolysis/hydrogenation of this invention may be maintained above 4.0 by merely the addition of caustic in view of the presence of acids with the cyclic aldehydes of this invention. At pH values below 4.0 the base metal hydrogenation catalyst life is surprisingly short as compared to values at 4.0 and above. Generally the upper pH limit in the process of the present invention for maintaining improved catalyst life is not critical. At pH values up to 6.9 an acceptable hydrogenation rate may be obtained. The upper limit on pH should be chosen to achieve a hydrolysis rate such that the reaction is completed in an acceptable length of time. Thus, while the pH range may be generally from 4.0 to 6.9, the preferred pH range is 4.0 to 5.5. Most preferably the pH is 4.0 to 4.5.

When the process of the present invention was used in a more narrow example the yield of 2-methyl-1,3-propanediol (MPD) was found to be extremely sensitive to pH. The yield of MPD as a byproduct can be substantially improved or maximized without a loss in yield of 1,4-butanediol by controlling the pH in the process of the present invention in the preferred range of 4.0 to 5.5, most preferably 4.0 to 4.5.

A mixture within the scope of this invention, 2(2' - propanal) - 4 - methyl - 1,3 - dioxane and 2(3' - propanal) - 4 - methyl - 1,3 - dioxane, is simultaneously hydrogenated and hydrolyzed in the presence of a nickel catalyst promoted with rhenium and aqueous sulfuric acid to yield 1,4-butanediol and 2-methyl-1,3-propanediol and recovered 1,3-butanediol. The control of the pH of the reaction mixture at from 4.0 to 5.5 greatly extends the life of the catalyst over that where the pH of the reaction mixture is below 4.0 and also, without a yield loss of 1,4-butanediol, produces increased yields of 2-methyl-1,3-propanediol.

Another mixture within the scope of this invention, 2(2' - propanol) - 4 - methyl - 1,3 - dioxane and 2(3' - propanol) - 4 - methyl - 1,3 - dioxane, is likewise simultaneously hydrogenated and hydrolyzed without a yield loss of 1,4-butanediol, produces increased yields of 2 - methyl - 1,3 - propanediol. It is also within the scope of this invention to use mixtures of 2(2' - propanal) - 5 - methyl - 1,3 - dioxane and 2(3' - propanal) - 5 - methyl - 1,3 - dioxane and mixtures of 2(2' - propanol) - 5 - methyl - 1,3 - dioxane and 2(3' - propanol) - 5 - methyl - 1,3 - dioxane.

The 1,4-butanediol prepared by the process of this invention may be separated from the byproduct diol(s) present therewith if desired. Where the diol is 2-methyl-1,3-propanediol, the separation with 1,4-butanediol is relatively simple due to the difference in boiling points. In any event, the byproduct diol(s) is separated from the 1,4-butanediol by conventional means.

As can be seen from the aforesaid cyclic acetal general formula the process of the present invention includes within its scope the step of prehydrogenating the acetal aldehydes in the presence of a hydrogenation catalyst to give compounds in which X is  $\text{—CH}_2\text{OH}$  prior to the simultaneous hydrolysis and hydrogenation in the presence of the base metal hydrogenation catalyst and aqueous acid according to the process of the present invention. This prehydrogenation is conducted at normal hydrogenation conditions, except for temperature, in the presence of a base metal hydrogenation catalyst. The prehydrogenation converts the  $\text{—CHO}$  groups to  $\text{—CH}_2\text{OH}$  before any hydrolysis of the starting compound.

The prehydrogenation, if desired, may be carried out in an aqueous medium in which case the water acts as a heat sink and a viscosity adjustor although the reaction can also be carried out neat; that is, without the use of water. If an

aqueous medium is used, it is convenient to have enough water present for the hydrolysis-hydrogenation step that follows.

The prehydrogenation is conducted at a temperature of from 40° to 125°C. Temperatures above 125°C will tend to promote simultaneous hydrolysis and hydrogenation.

The pressure for the prehydrogenation is generally from 500 to 10,000 psig, preferably 1,000 to 5,000 psig.

The prehydrogenation results in the preparation of compounds with the aforesaid general formula where X is CH<sub>2</sub>OH. Thus, the process of the present invention comprises the simultaneous catalytic hydrogenation and hydrolysis at a pH of 4 to 5.5 of compounds of the general formula given above where X is —CHO as well as where X is —CH<sub>2</sub>OH.

The process of the present invention is further described by reference to specific cyclic acetals. It will be understood, however, that the process of the invention is equally applicable to the cyclic acetals of the general formula given above.

The cyclic acetals of the present invention may be prepared by the reaction of a diol having at least three carbon atoms and a maximum of three carbon atoms separating the diol hydroxy groups with at least a stoichiometrically equivalent quantity of an unsaturated aldehyde after which hydroformylation produces the cyclic acetals. British Specification 1,460,869 discloses the preparation of the cyclic acetals. U.S. Patents 3,963,754 and 3,963,755 disclose the preparation of 2(3' - propanal) - 5 - methyl - 1,3 - dioxane and 2(2' - propanal) - 5 - methyl - 1,3 - dioxane. Other cyclic acetals may be prepared according to the disclosure in the aforesaid patents. The starting compounds of this invention of the aforesaid general formula where X is CH<sub>2</sub>OH may be prepared by the hydrogenation of the cyclic acetals aldehydes under hydrogenation conditions described herein in the presence of the base metal hydrogenation catalysis of this invention also indicated herein as prehydrogenation.

The process of the invention is useful in the preparation of 1,4-butanediol which can be converted to tetrahydrofuran both of which are useful as solvents.

The examples were all conducted with the indicated 4-methyl aldehydes (from the readily available 1,3-butanediol) rather than the 5-methyl aldehydes (from the less readily available MPD). Tests, however, indicate no major differences between the performance of the 4-methyl aldehydes and the 5-methyl aldehydes.

The following examples further illustrate the invention. All percentages are by weight unless otherwise indicated.

#### EXAMPLE 1

A 100 g sample of nickel catalyst was charged to a 1—1/2" diameter high pressure tubular reactor. To this was fed 85% 2(3' - propanal) - 4 - methyl - 1,3 - dioxane and 15% 2(2' - propanal) - 4 - methyl - 1,3 - dioxane and H<sub>2</sub>O at a 2:1 weight ratio of acetal to water at 270 ml/hr together with a 5:1 weight ratio of recycle of reactor product to acetal and water feed. The hydrogenation catalyst bed was maintained at 155°C and 2,000 psig H<sub>2</sub> pressure.

The catalyst was 50% Ni on kieselguhr and no attempt was made to control pH. The initial pH of the product was 5.0, but after one day the pH fell below 4.0 at which time the catalyst activity fell to less than half of its original value.

#### EXAMPLE 2

The procedure of Example 1 was followed except that the pH of the reactor mixture was maintained at 5.0 to 5.5 by addition of a small amount of NaOH via the H<sub>2</sub>O feed (0.006N NaOH) throughout the reaction. The catalyst survived for eight days before it suddenly lost most of its activity. The yield of 1,4-butanediol remained constant for the first eight days at the run at 85%. However, at that point the yield declined rapidly down to 54% indicating a loss in catalyst activity.

#### EXAMPLE 3

The procedure of Example 1 was followed except that the catalyst was 1/8 inch diameter pellets of 50% Ni on alumina and no control was exerted over pH. The initial pH of the reactor mixture was 5.0. Over the first four days the pH gradually drifted down to 4.0, but the activity remained at its original high value. On the fifth day, the pH fell below 4.0, and the catalyst lost more than half of its original activity as determined by the loss of yield of 1,4-butanediol and MPD to about 50% of the yield of the first four days.

## EXAMPLE 4

The procedure of Example 1 was followed except that the catalyst was prepared by adding a solution of 5.0 g  $\text{Re}_2\text{O}_7$  in 25 ml  $\text{H}_2\text{O}$  to a fresh 100 g sample of the same Ni on alumina catalyst used in Example 3. The solution was completely absorbed by the catalyst. The catalyst was placed in the reactor and treated with  $\text{H}_2$  at 1 atm at  $180^\circ\text{C}$  for 2 hours to reduce and insolubilize the  $\text{Re}_2\text{O}_7$ . During this run the pH was controlled at 4.0 to 5.5 by addition of NaOH to the water feed (0.0012N NaOH). This run was carried out for 19 days, and there was no significant loss of catalyst activity. The effect of pH on yield of 1,4-butanediol, 2-methyl-1,3-propanediol (MPD), branched and linear hydroxy acetal is summarized in the table that follows:

Percent Yields

pH	MPD	BHA	Total Branched	1,4-BAD	LHA	Total Linear
5.4	38	46	80	68	19	87
5.3	32	38	70	71	16	87
5.0	55	30	85	79	11	90
4.6	65	17	82	83	5	88
4.5	78	15	93	87	3	90
4.3	85	6	91	89	1	90
4.1	85	4	89	87	1	88
4.1	85	4	89	89	1	90

MPD=2-methyl-1,3-propanediol

BHA=branched hydroxyacetal

1,4-BAD=1,4-butanediol

LHA=linear hydroxyacetal

Thus, it can be seen that the yield of MPD decreases with increasing pH. While the unreacted BHA yield loss can be overcome with further hydrolysis and hydrogenation to MPD with extended reaction times, this would be disadvantageous.

## EXAMPLE 5

The procedure of Example 1 was followed, except the catalyst was 200 g of Raney nickel (25% aluminum removed). During the run the pH was maintained at 4.5 to 5.0 by addition of NaOH with water feed. The run was carried out for 10 days during which time the yield of 1,4-butanediol was between 85 and 87%, the MPD yield was between 70 to 85%, and the catalyst showed no sign of loss of activity.

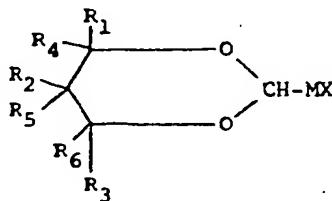
## EXAMPLE 6

The procedure of Example 4 was repeated except that the particle size of the catalyst of Example 3 was decreased to 1/16 inch diameter particles. The run was carried out for 55 days. The activity of the catalyst began to decrease after about 35 days as evidenced by a decrease in BAD and MPD yield. The pH was controlled at 4.0 to 5.0. The yield of BAD for the first 45 days was greater than 95% while the MPD was 85 to 100% for the first 35 days.

While the invention has been described in considerable detail in the foregoing, it is to be understood that such detail is solely for the purpose of illustration and that variations can be made by those skilled in the art.

## WHAT WE CLAIM IS:—

1. A process for the simultaneous catalytic hydrolysis and hydrogenation of a cyclic acetal of the general formula



or mixtures thereof,

wherein M is an alkylene group of 1 to 20 carbon atoms, X is —CHO or —CH<sub>2</sub>OH and R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub> may be the same or different hydrogen or alkyl groups of 1 to 20 carbon atoms, which comprises hydrolyzing and hydrogenating simultaneously said acetal at an elevated temperature under superatmospheric hydrogen pressure in the presence of an aqueous acid solution and a base metal hydrogenation catalyst, and maintaining a pH of 4.0 or more until a product comprising a diol or mixture of diols is prepared.

2. A process as claimed in claim 1 wherein the pH is maintained at from 4.0 to 5.5.

3. A process as claimed in claim 1 wherein the pH is maintained at from 4.0 to 4.5.

4. A process as claimed in any one of the preceding claims wherein the base metal hydrogenation catalyst is nickel, conventional Raney nickel, conventional Raney nickel promoted with molybdenum, conventional Raney nickel promoted with chromium, granular foraminous nickel, granular foraminous nickel promoted with molybdenum or granular foraminous nickel promoted with chromium.

5. A process as claimed in any one of claims 1 to 3 wherein the base metal hydrogenation catalyst is granular foraminous nickel.

6. A process as claimed in any one of claims 1 to 3 wherein the base metal hydrogenation catalyst is conventional Raney nickel.

7. A process as claimed in any one of claims 1 to 3 wherein the base metal hydrogenation catalyst is conventional Raney nickel promoted with molybdenum or chromium.

8. A process as claimed in any one of claims 1 to 3 wherein the base metal hydrogenation catalyst is granular foraminous nickel promoted with molybdenum or chromium.

9. A process as claimed in any one of the preceding claims wherein the base metal hydrogenation catalyst is treated with rhenium prior to its use in this process.

10. A process as claimed in any one of the preceding claims wherein X is —CHO.

11. A process as claimed in claim 10 wherein the cyclic acetal starting material is a mixture of 2(3' - propanal) - 5 - methyl - 1,3 - dioxane and 2(2' - propanal) - 5 - methyl - 1,3 - dioxane and the product is 1,4 - butanediol and 2 - methyl - 1,3 - propanediol.

12. A process as claimed in any one of claims 1 to 10 wherein the cyclic acetal starting material is a mixture of 2(3' - propanal) - 4 - methyl - 1,3 - dioxane and 2(2' - propanal) - 4 - methyl - 1,3 - dioxane and the product is 1,4-butanediol, 2 - methyl - 1,3 - propanediol and 1,3 - butanediol.

13. A process as claimed in any one of claims 1 to 9 wherein X is —CH<sub>2</sub>OH.

14. A process as claimed in claim 13 wherein the cyclic acetal starting material is a mixture of 2(3' - propanol) - 5 - methyl - 1,3 - dioxane and 2(2' - propanol) - 5 - methyl - 1,3 - dioxane and the product is 1,4-butanediol and 2 - methyl - 1,3 - propanediol.

15. A process as claimed in any one of the preceding claims wherein the reaction temperature is from 125 to 200°C.

16. A process as claimed in any one of the preceding claims wherein the reaction pressure is 500 to 10000 psig.

17. A process as claimed in claim 1 substantially as described herein in any one of the Examples.

18. A diol when produced by a process as claimed in any one of the preceding claims.

19. 1,4-butanediol when produced by a process as claimed in any one of the preceding claims.

For the Applicants,  
FRANK B. DEHN & CO.,  
Chartered Patent Agents,  
Imperial House,  
15—19 Kingsway,  
London, WC2B 6UZ.